

AD-A244 386



2

Final Technical Report

for

Electrochemically Modulated Superconductivity

To:

Office of Naval Research
800 North Quincy Street
Arlington, VA 22217-5000

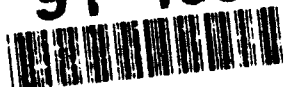
From:

Materials Processing Center
Massachusetts Institute of Technology
Cambridge, MA 02139-4307

Professors Donald R. Sadoway
and
Robert M. Rose
Principal Investigators

Contract No. N00014-90-J-1722
R&T Project No. s400015src03
Contract Period: March 1, 1990 - August 31, 1991
Program Manager: Dr. Fred Quelle
Date: November 26, 1991

91-16858



91 1 04 021

Goal

The goal of this project was to test the feasibility of electrochemically modulated superconductivity in the cuprate superconductors. Such a test is possible because the new high temperature superconductors are ionic solids that are extremely sensitive to oxygen potential. Passive optimization of the latter is impossible, not only due to materials processing limitations but also due to thermodynamic and structural instabilities. Our approach is active intervention by electrochemical means, in other words, electrochemical polarization while the material is actually or potentially in the superconducting state. This requires electrolytes that are functional at cryogenic temperatures. Several years ago we discovered cryogenic electrolysis and demonstrated the existence of such remarkable media. Success in this effort would make possible a new class of electronic and photonic devices that exploit the capability to control actively the transition into and out of the superconducting state while the material is in service.

Approach

A cuprate-based superconductor is polarized electrochemically in a cryogenic electrolyte while the electrical resistivity is measured simultaneously.

Tasks

1. Selection of candidate electrolyte. Such an electrolyte should be liquid and conduct electricity at temperatures below 95 K, and should not interact otherwise with the cuprate superconductors (e.g., hydrolysis, as would occur at room temperatures in aqueous electrolytes, is not acceptable). Initial choices for evaluation were:

- * ozone/oxygen
- * carbon monoxide
- * trifluoronitrosomethane/Freon 14
- * trifluoramine oxide/trifluoramine
- * chlorotetroxyfluoride/Freon 14
- * nitropropane/propane
- * sulfur dioxide/propane
- * nitryl chloride/Freon 14
- * carbonyl sulfide/propane
- * allyl alcohol/dimethyl ether

Statement A per telecon
Dr. Yoon Soo Park ONR/Code 1212
Arlington, VA 22217-5000

NWW 1/13/92

These candidates consisted of an oxidizable species and a solvent. Some of the oxidizable compounds are liquid at 95 K, but most have to be dissolved in a low melting solvent such as Freon 14 or propane.

2. Construction of a test cell. Problems include the fact that condensed ozone is a high explosive.

Codes

Dist

Avail and/or
Special

A-1

3. Screening experiments for candidate electrolytes, including electrical conductivity, emf measurements, cyclic voltammetry and ultimately laser Raman spectroscopy.

4. Electrochemical polarization of cuprate superconductors, based on the preceding steps.

Accomplishments

Cryoelectrochemical Cells

Cell design #1: Because of difficulties with ohmic connections to the superconductor (simultaneous 4-point probe resistance measurement and electrochemical polarization requires five leads which are stable in the electrolyte, reducing the odds considerably for success in any given run) we designed a non-contact method to detect superconductivity in a specimen while it is being actively polarized in the electrochemical cell. The coil (sketch, Figure 1) sits outside the working electrode but within the inner wall of the cryostat. The design, an inverted pancake geometry, has excellent sensitivity at audio frequencies and has been successfully tested with superconducting samples in the cell geometry but without electrochemical modulation. The cryostat is in essence a copper can with appropriate plumbing for introduction of gases and liquids and electrical feedthroughs for thermometry, susceptometry and electrochemical experiments.

Cell design #2: To test the detection limits, spacers were used to linearly vary the distance between the BYCO electrode and the pancake coil. Detection of the superconducting transition was possible at a distance of 0.29 inches from the coil. See Figures 2, 3 and 4.

Cell design #3: A cell has been designed to test ionic conductivity. The cell takes into account the expected high resistance of the electrolyte by having a guard electrode to eliminate stray capacitances. It is also equipped with a "piston" working electrode to vary in a controlled manner the distance between the electrodes. Ports on the working electrode allow electrolyte to flow into or out of the space between the electrodes. See Figure 5.

Cell designs #4 & 5: Cells 4 and 5 are designed for both conductivity measurements and electrochemical experimentation. Concentric rings on the working electrode (Figures 6 and 7) allow for approximately equal area electrodes for conductivity measurements, while at the same time allowing for a significantly smaller working electrode in electrochemical measurements. Inlets are provided for two reference electrodes to assure their reliability prior to measurements. Two platinum resistance thermometers may be used to test for temperature uniformity in the electrolyte. As mentioned above, guard electrodes eliminate stray capacitances. In cell 4 the working electrode is mobile with electrolyte both above and below it. In cell 5 (Figure 8), the working electrode is stationary and at the cell bottom allowing easier (re)placement of the working electrode with either a platinum test electrode or a BYCO one. Cell #5 also confines the electrolyte between two electrodes.

Cell design #6, 7 & 8: Cells 6, 7 and 8 are designed to test the reliability of a candidate reference electrode. Cell #6 (Figure 9) is fitted with 5 ports, one for a platinum resistance thermometer, and four for the reference electrode lead wires. In this cell open circuit voltages and voltage versus current measurements can be made at different isotherms over the liquid range of the electrolyte. Cell #7 (Figure 10) is designed to allow one reference electrode to be isolated from the rest. Open circuit voltages are measured between the isolated electrode and the three remaining electrodes to determine junction potentials. A platinum resistance thermometer (RTD) is also present so that junction potentials may be measured at various isotherms. The last cell (Figure 11) is designed to measure the changes in the equilibrium potential of the reference electrode with temperature. One electrode, either a candidate electrode or a saturated calomel electrode, is held at room temperature at the top. A candidate electrode is fitted to be in the lower part of the cell where its temperature is varied over the liquid range of the electrolyte. Two RTD's are placed in this cell, one at the top and one at the bottom to monitor the temperature difference while measuring the open circuit potential difference. The cell length is designed to accommodate the precipitation at solute as the temperature is lowered.

Screening Experiments

Two candidate electrolyte systems have been investigated for electrochemical measurements:

1) Oxygen-ozone solutions. The liquid range for oxygen is 54.75-90.19 K, while ozone is liquid from 80.45 to 161.25 K. Using an electrical discharge apparatus constructed for this purpose, we have produced solutions of approximately 2% ozone in oxygen. We have performed surface tension measurements to confirm that this solution wets barium yttracuprate. No visible chemical reactions of this solution with the barium yttracuprate have been observed, although subtler interactions may have occurred. We have made preliminary measurements which indicate no measurable ionic conductivity in this solution, that is to say, it does not appear to be an electrolyte, at least in the conventional sense of the word. However, as large scale electron transfer is not required to meet the stated goals of this project, this solution is still a candidate owing to anticipated electron sharing with the double layer along with the associated band bending in the solid.

2) Butyronitrile (BN) - chloroethane (CE) mixtures. These were discovered during the course of this investigation and were not on the original list of candidate electrolyte systems. The liquid range of BN is 161 to 389 K, while CE is a liquid from 135 to 285 K. This mixture has a solidification minimum at approximately 90 K¹. The addition of increasing quantities of CE (from 1:1 to 1:2) broadens it. The addition of electrolyte further depresses the melting point¹. It is also suspected that glassification occurs beginning at

¹ S. Ching, J.T. McDevitt, S.R. Peck, and R.W. Murray, *J. Electrochem. Soc.*, 138(8), August, 1991, pp. 2308-2315.

approximately 110 K¹. From the literature, cyclic voltammetry, in a 1:2 mixture, has been conducted at temperatures as low as 88 K with potential window of ± 3 V at 113 K. Conductivity measurements of this solution with a tetrabutylammonium salt at temperatures as low as 113 K have also been reported. Impurities include unsaturated nitriles and water. By distillation, water can be reduced to 3 mM. The unsaturated nitriles are suspected of narrowing the anodic/cathodic limits.

Electrochemical Experiments

Electrochemical Modulation of BYCO Material.

Oxygen-ozone solutions. Though not a conventional electrolyte, meaning there is no detectable ionic conductivity, polarizations of BYCO versus a copper mesh were conducted in this solution as it was anticipated that electron sharing with the double layer along with the associated band bending in the solid would be sufficient to modify the BYCO's properties (Figure 12). DC voltages up to ± 120 V were applied between the BYCO working electrode and the copper counter electrode while the superconducting properties of the BYCO material were monitored with the pancake coil. (See figures 13 and 14.) In these figures, the X-axis is temperature measured in Ohms. (1 Ohm is approximately 3K.) The two Y-axis measure the real and imaginary components of susceptibility. The peak in the imaginary component indicates the eddy currents -- a sign of a superconducting transition. The real part indicates an imbalance between the balanced secondaries of the pancake coil, also an indication of superconductivity. No change in properties as manifested in the magnetic susceptibility was observed with applied potential.

Reference Electrode Testing.

Butyronitrile-chloroethane solutions. At present a suitable reference electrode for this system is sought. In acetonitrile, which is a chemical relative of BN, Ag/AgCl is reported to be a reliable reference electrode. Accordingly, it was the first candidate. (See figures 15 and 16.) At room temperature V vs. I is linear, as is expected of a good reference electrode. As the temperature is dropped, open circuit voltages between pairs of electrodes were neither close to zero nor consistent between two separate pairs indicating that this is not a reliable reference electrode. Therefore, a second candidate has been selected based on the ferrocene-ferrocenium couple. The ferrocenium source will be ferrocenium iodide.

Conclusions

- 1) The search for electrolytes functional at superconducting temperatures, i.e., 90 K in the case of BYCO, has resulted in the discovery of such media. The search for reference electrodes operative at cryogenic temperatures has been much more difficult. To date, no fully satisfactory reference electrode has been certified. However, not all options have been exhausted.

- 2) In our limited experience we have not been able to demonstrate electrochemical modulation of superconducting behavior in BYCO material. However, it is important to recognize that this is not due to any intrinsic physical limitation. In other words, nothing in our research points to the impossibility of the phenomena. Rather, it is a question of discovering the right set of conditions to make it happen. Further research may prove to be successful.

Recommendations for Future Work

1. Continue evaluation of electrolytes in terms of their physical chemistry and electrochemistry. Recommended techniques are thermal analysis to obtain phase diagrams of multicomponent solutions and electrochemical impedance spectroscopy to measure electrical conductivities.
2. Electrochemical studies to evaluate and characterize the electrode processes, including electromotive force measurements, cyclic voltammetry, electrochemical impedance spectroscopy, and laser Raman spectroscopy performed *in situ* at the electrode-electrolyte interface.
3. Electrochemical modulation experiments.

Detection Distance of BYCO Sample from Coil

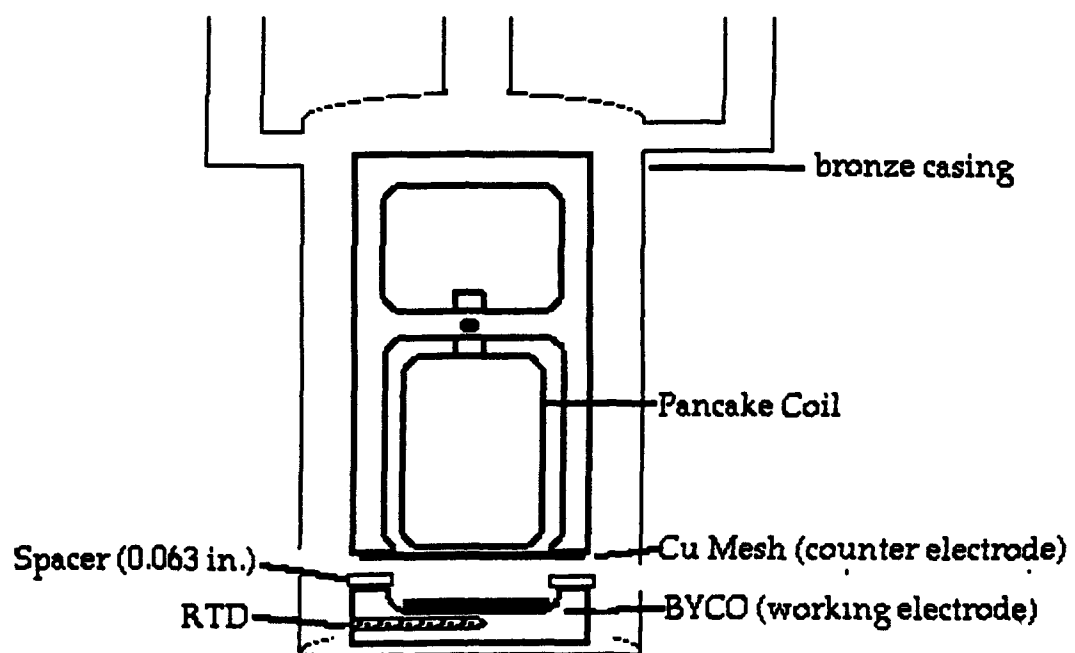


Figure 1

Detection of Superconductivity verses Distance from Coil

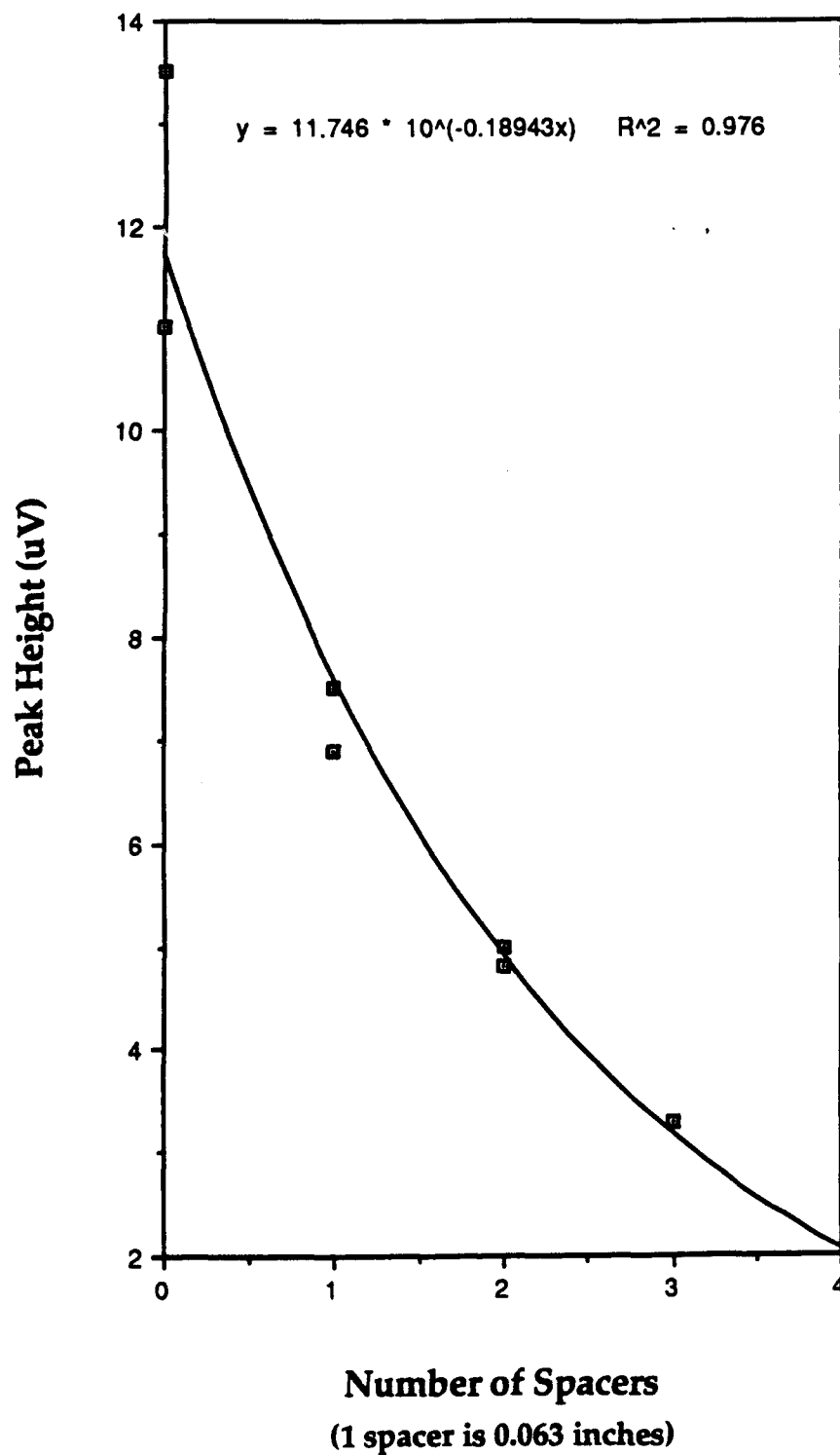
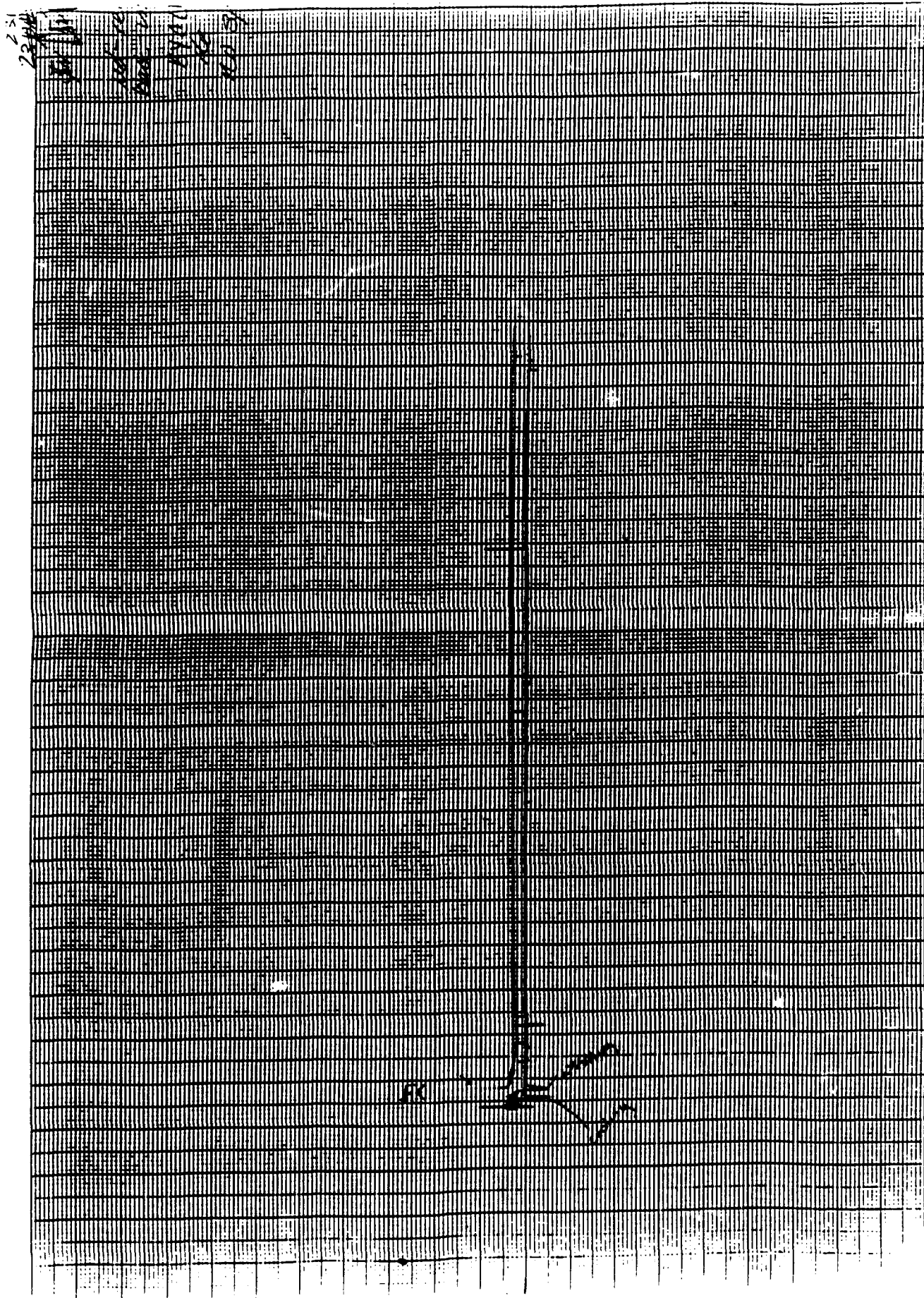
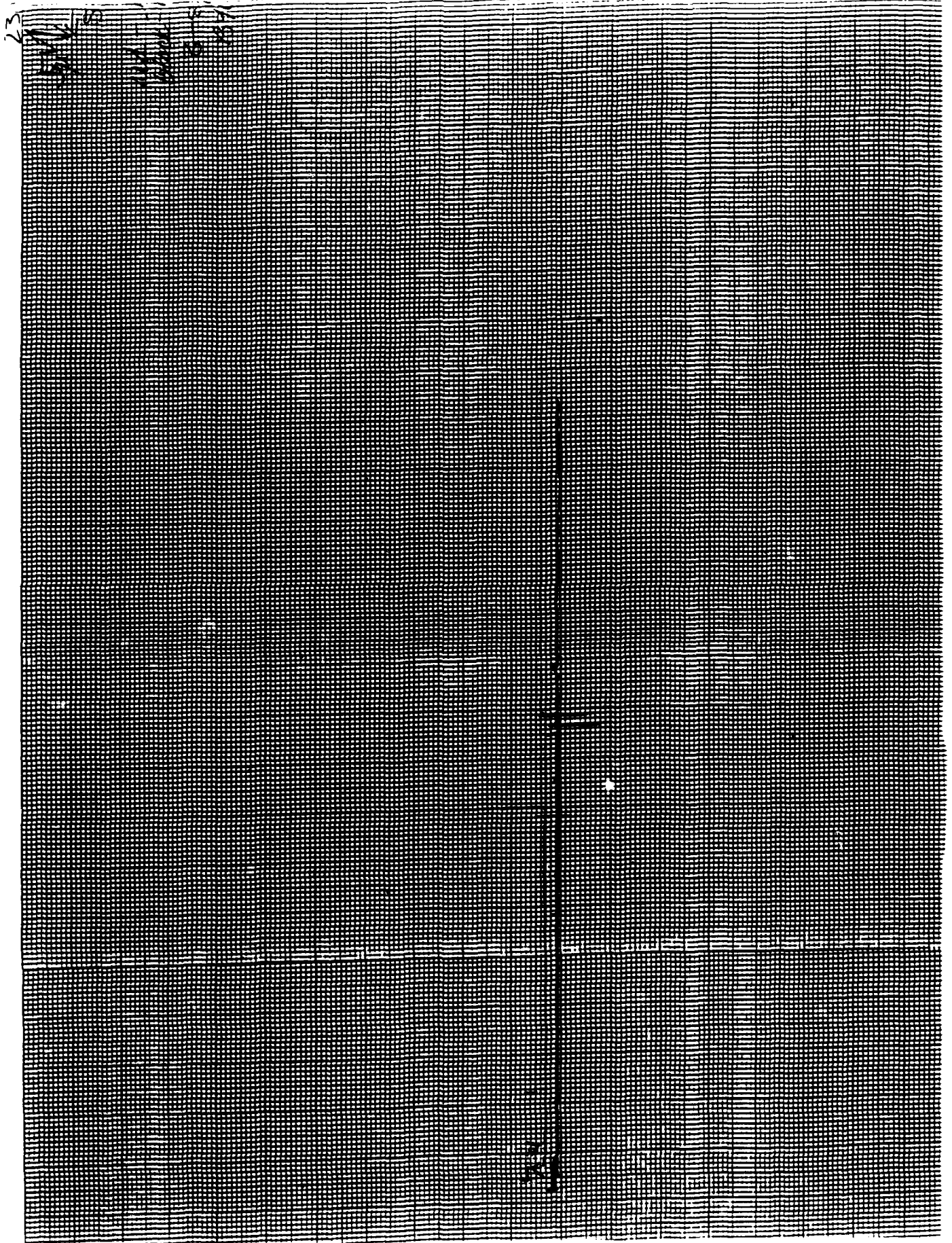


Figure 2





Conductivity Cell Cell Design #3

*Note: the working
electrode is on a
piston to vary electrode
spacing

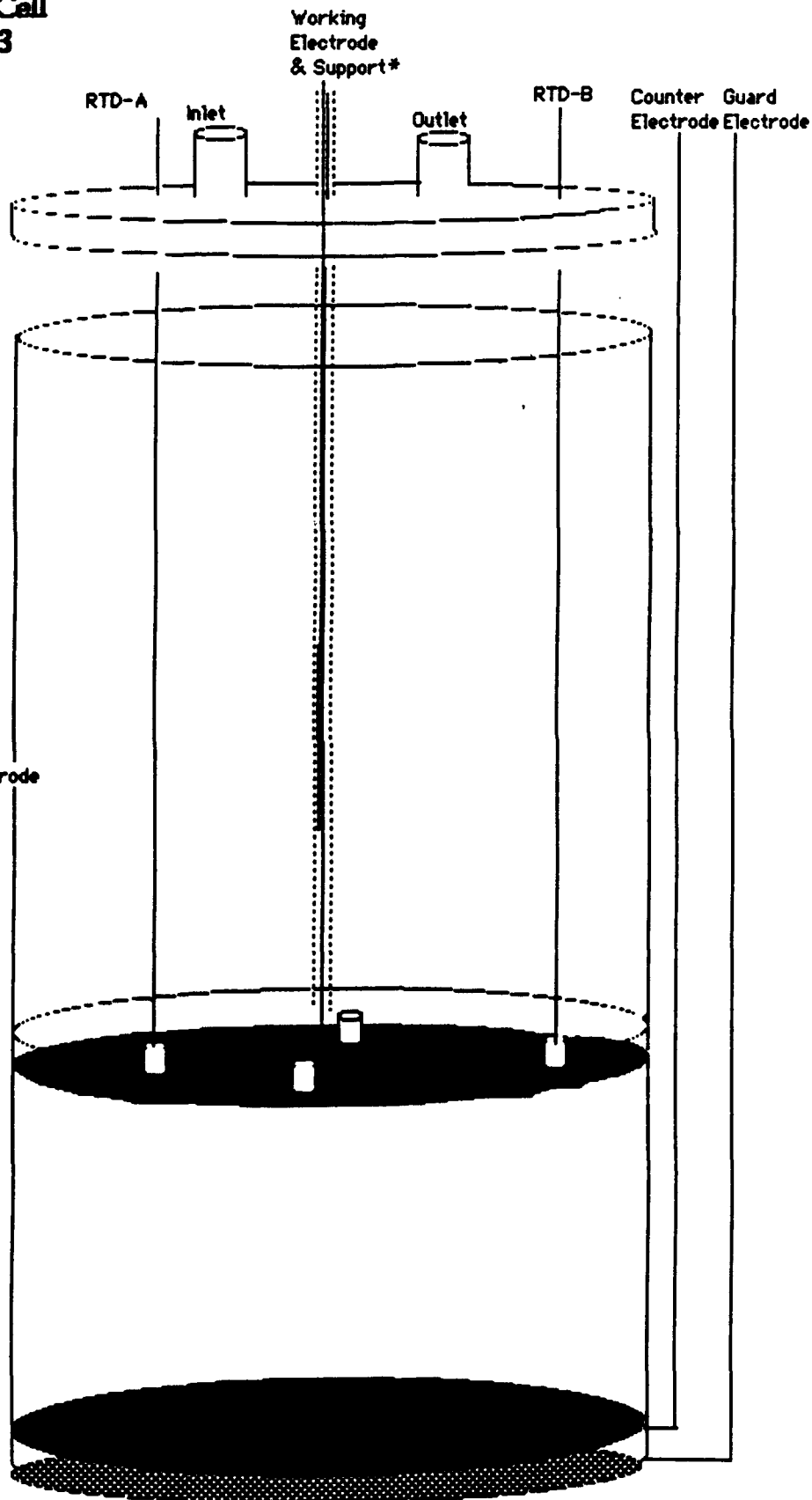


Figure 5

Bottom of Conductivity/Electrochemistry Cell

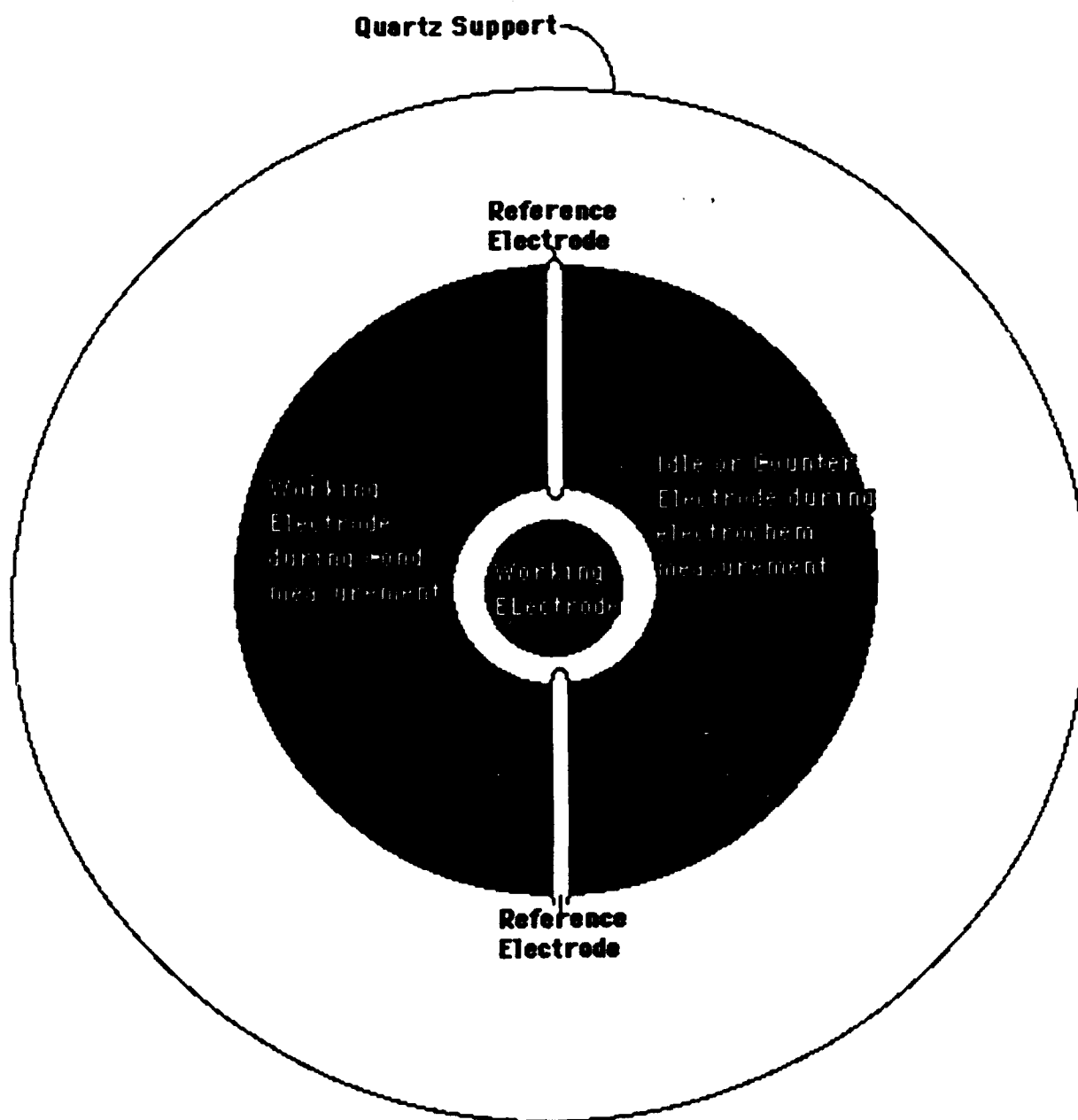
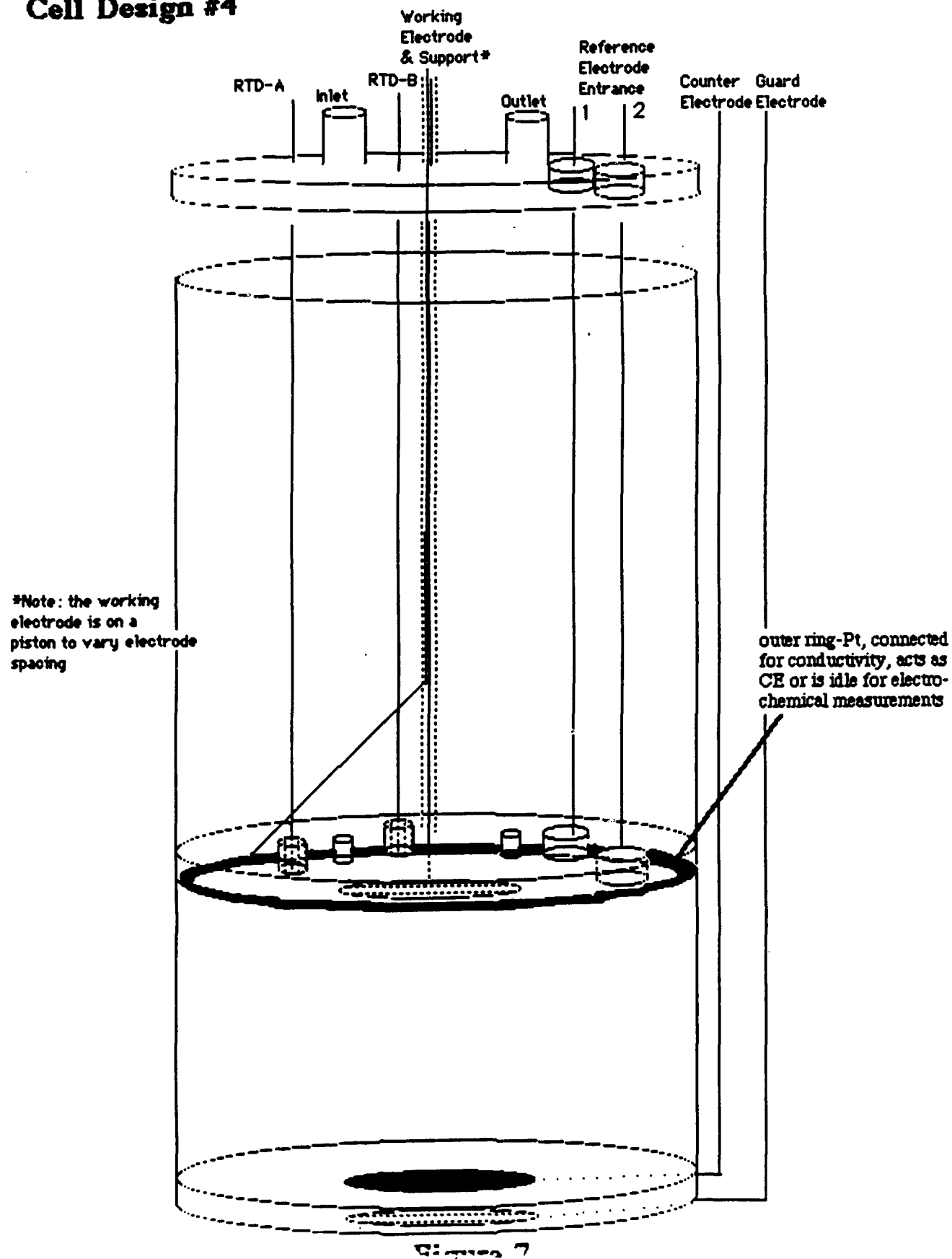
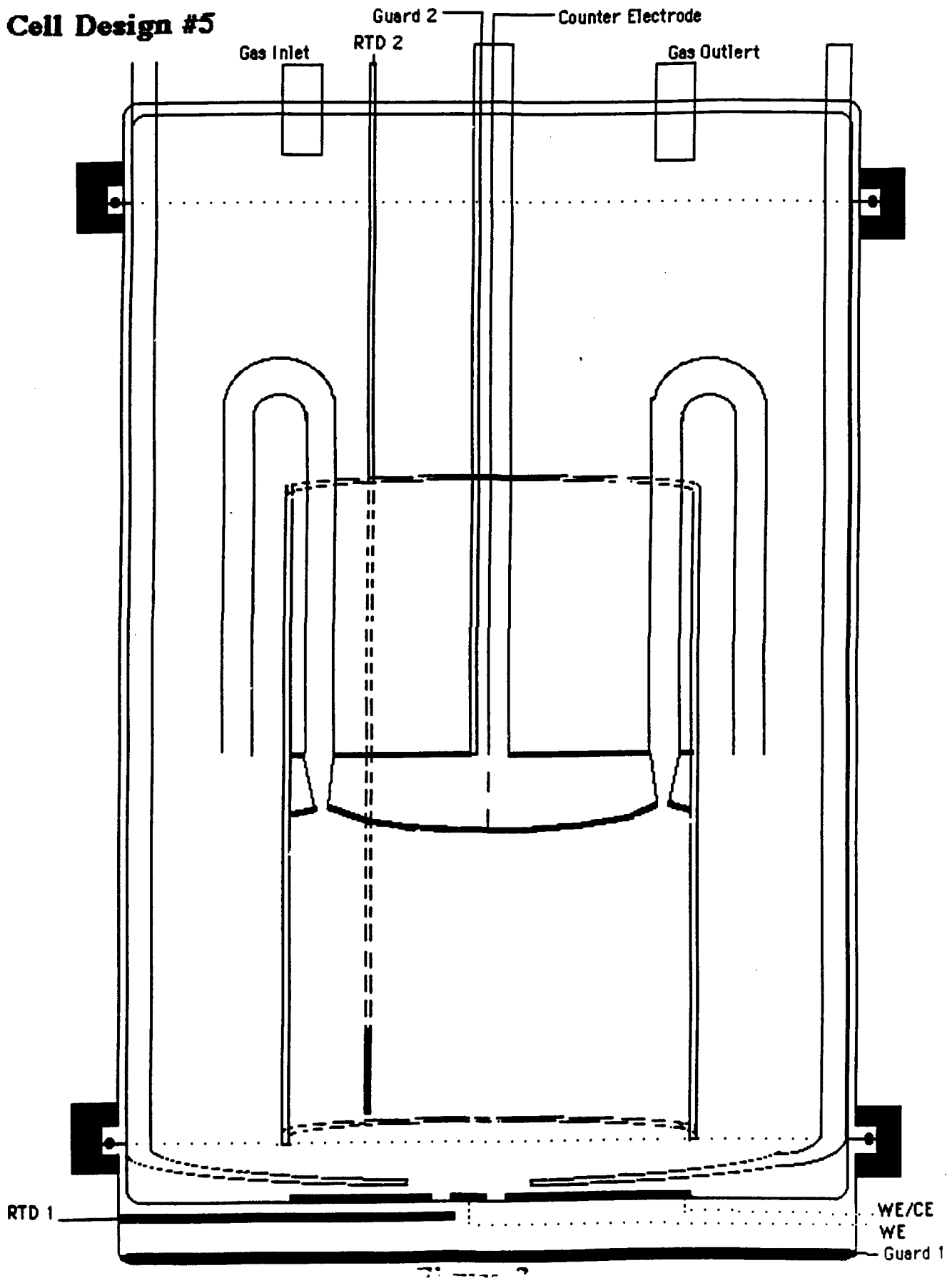


Figure 6

Cell Design #4

Cell Design #5



Reference Electrode: Cell Design #6

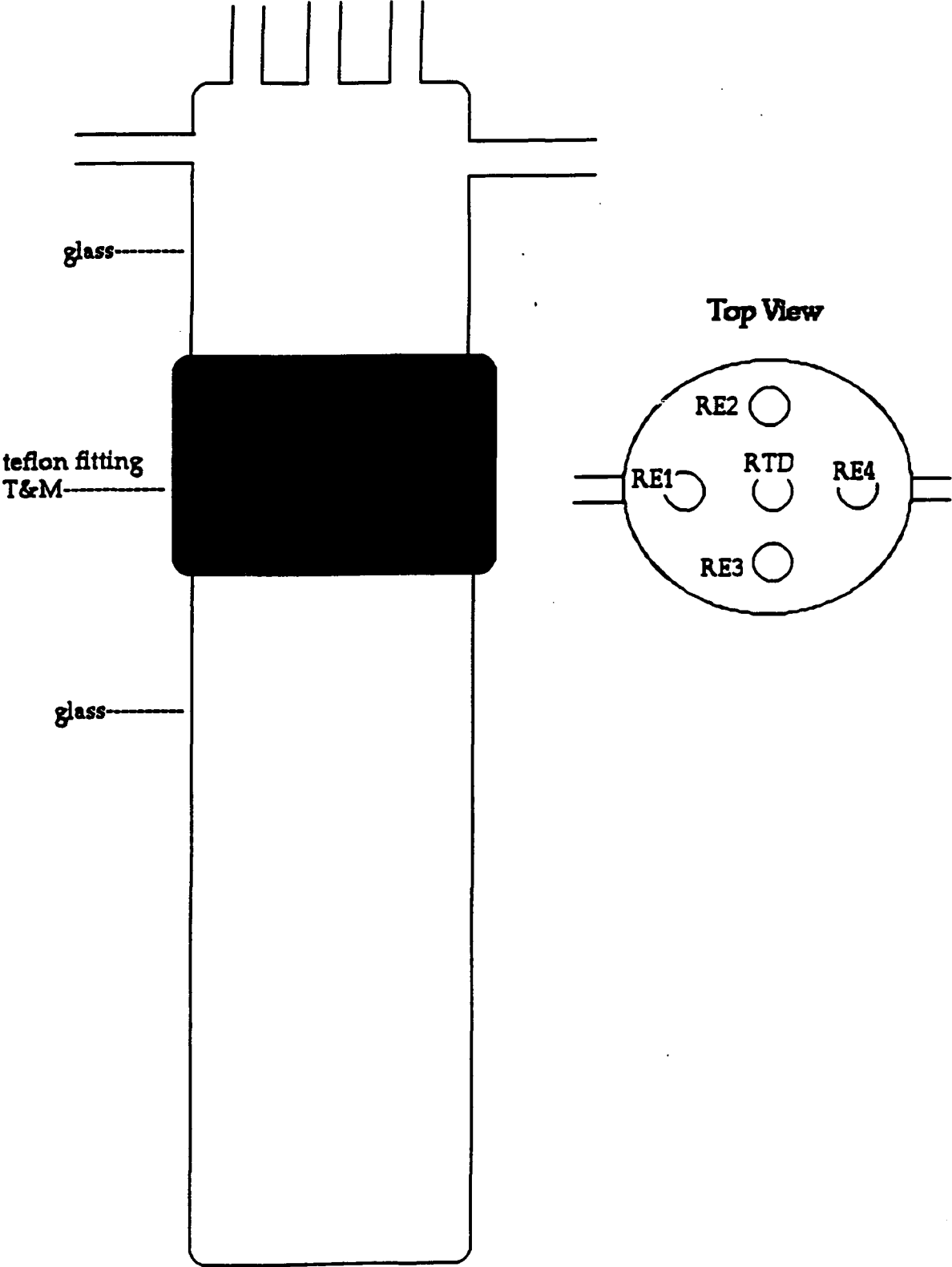


Figure 9

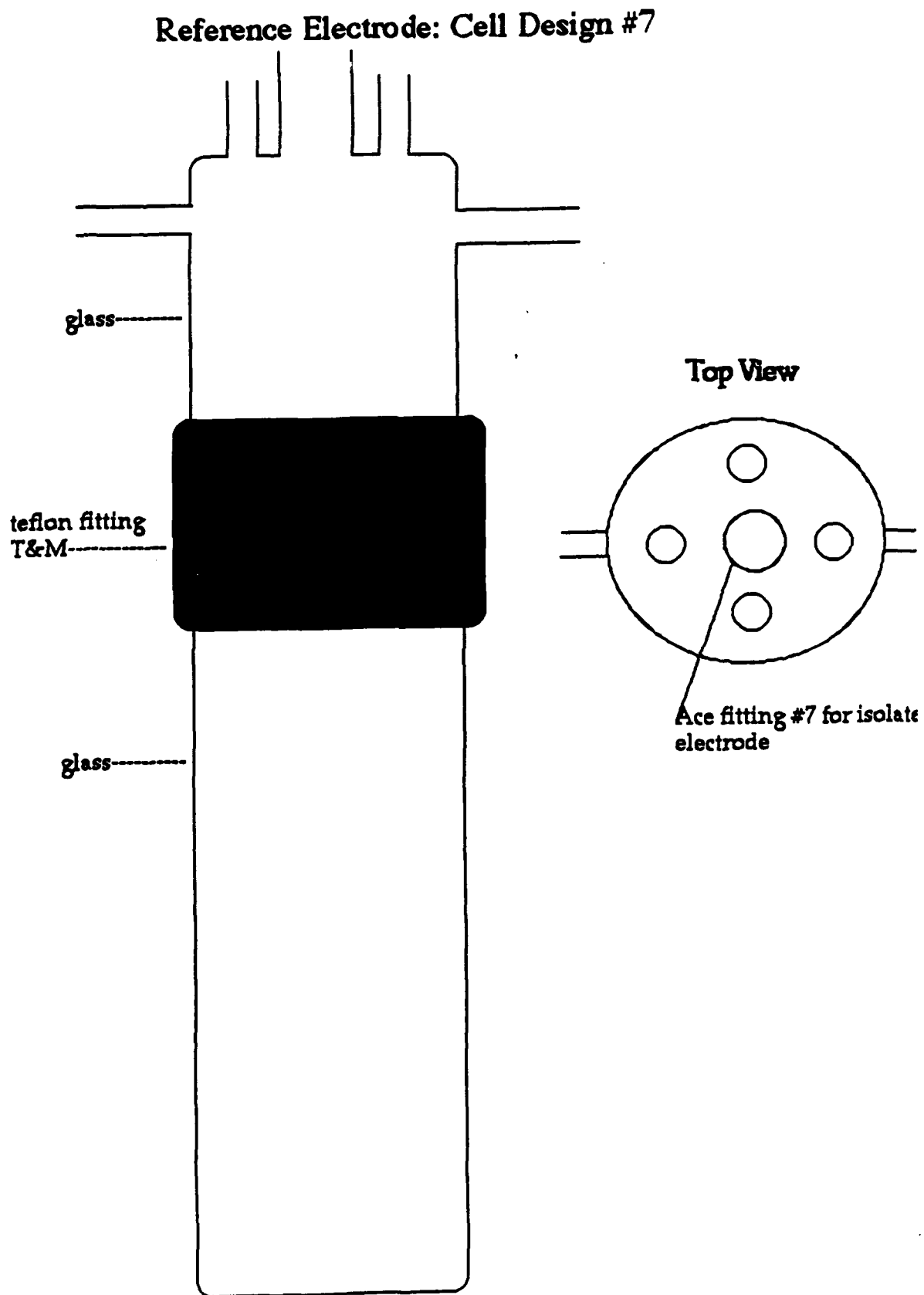


Figure 10

Reference Electrode: Cell Design #8

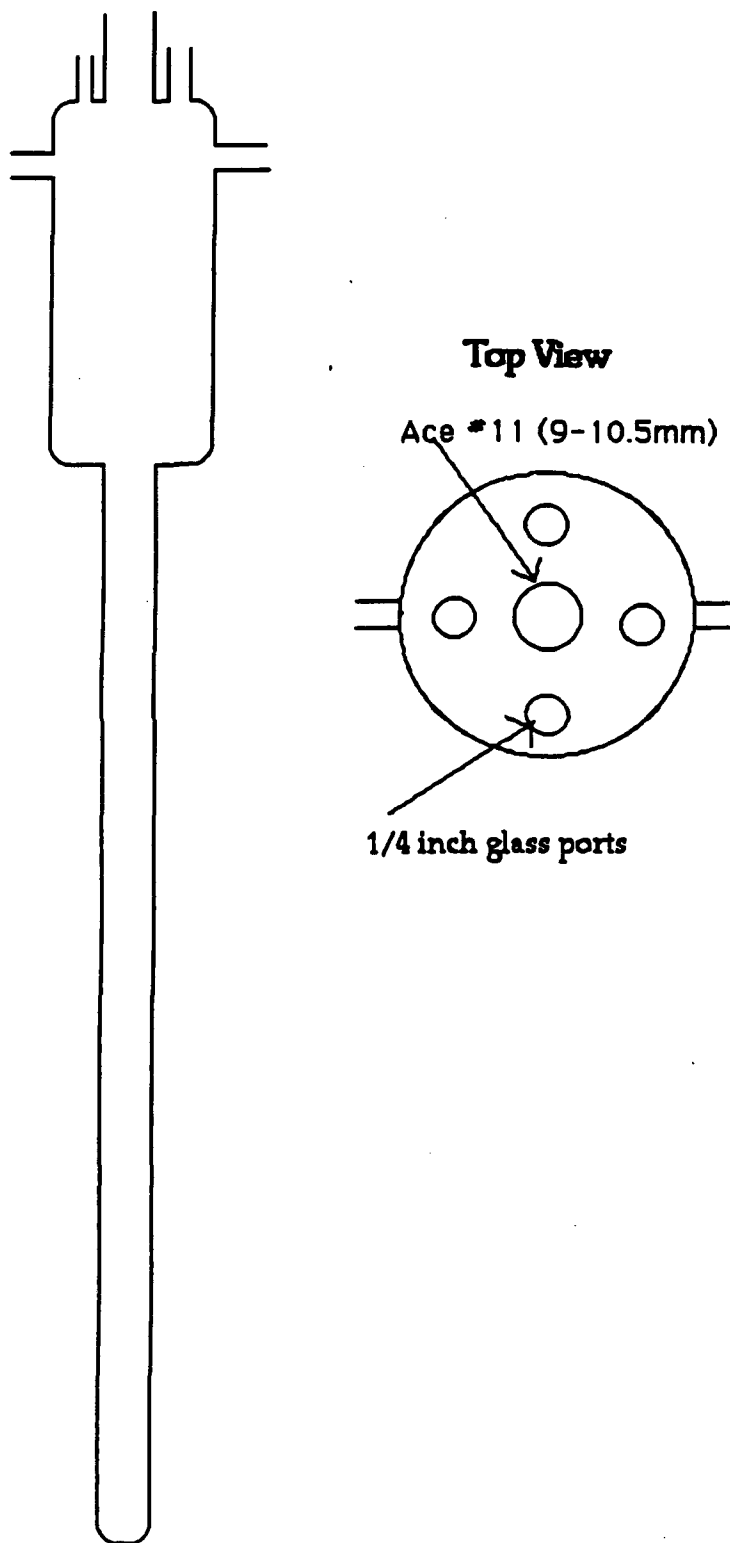
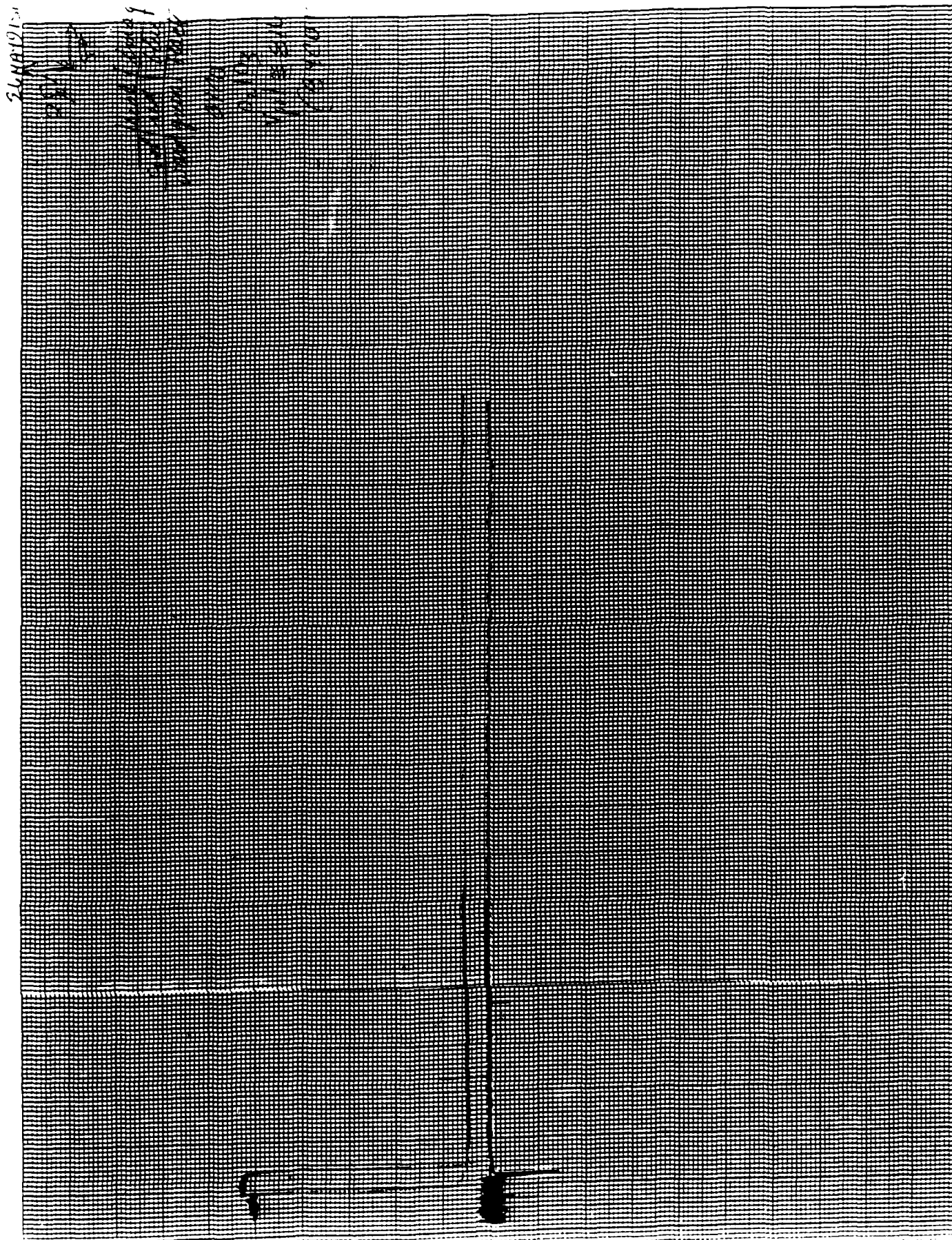
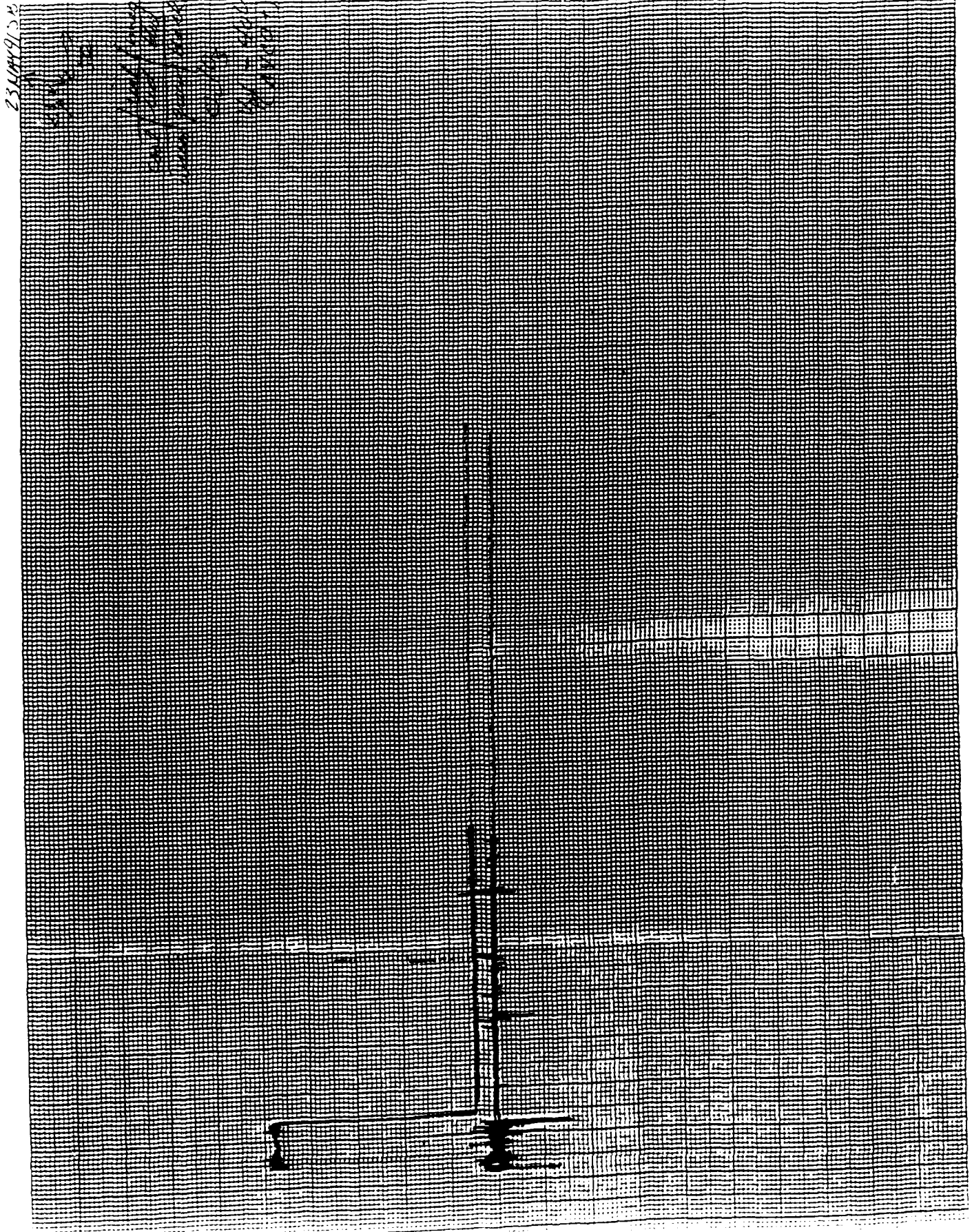


Figure 11





Voltage vs Current in TMAC Butyronitrile Ag/AgCl Reference Electrodes at Room Temperature

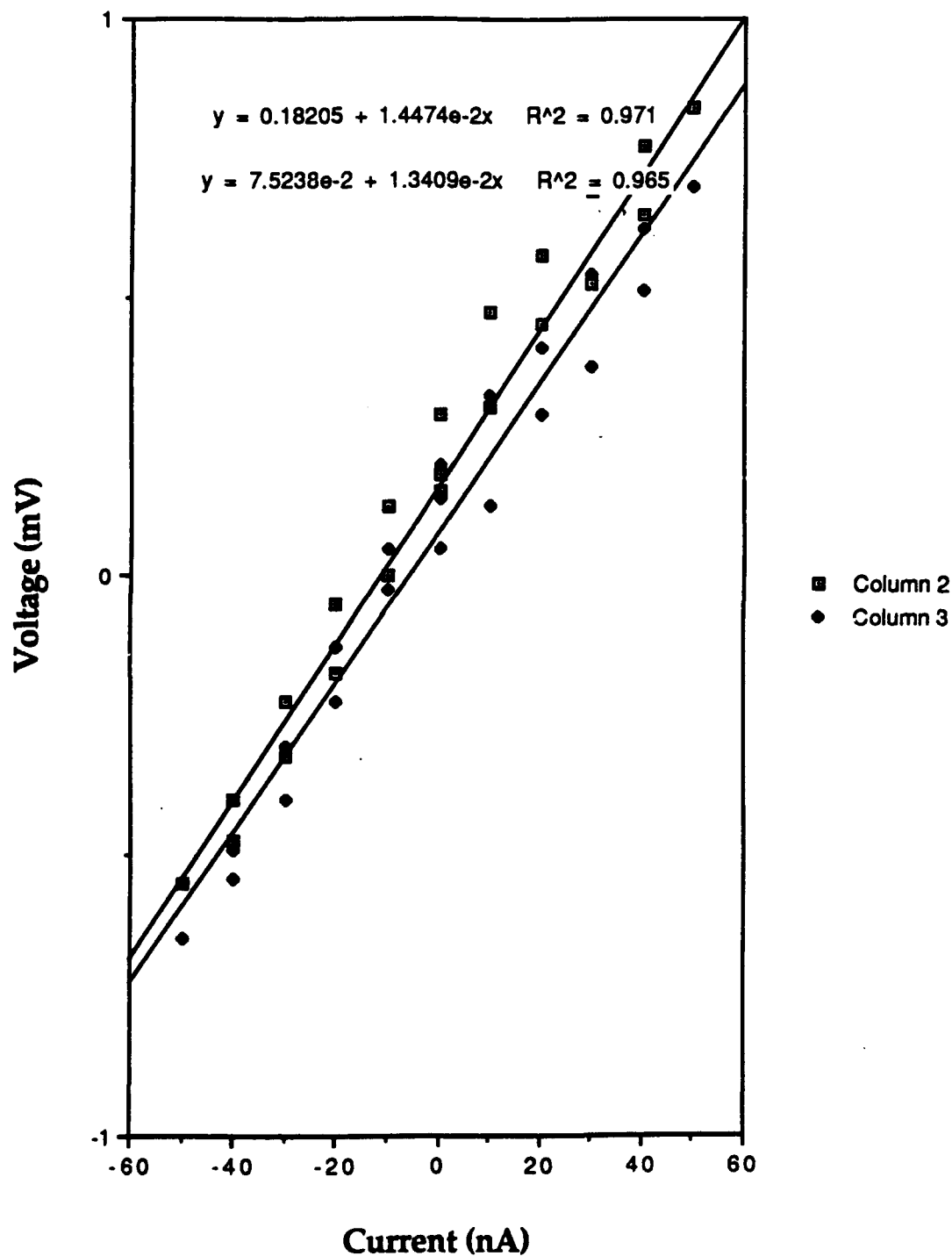
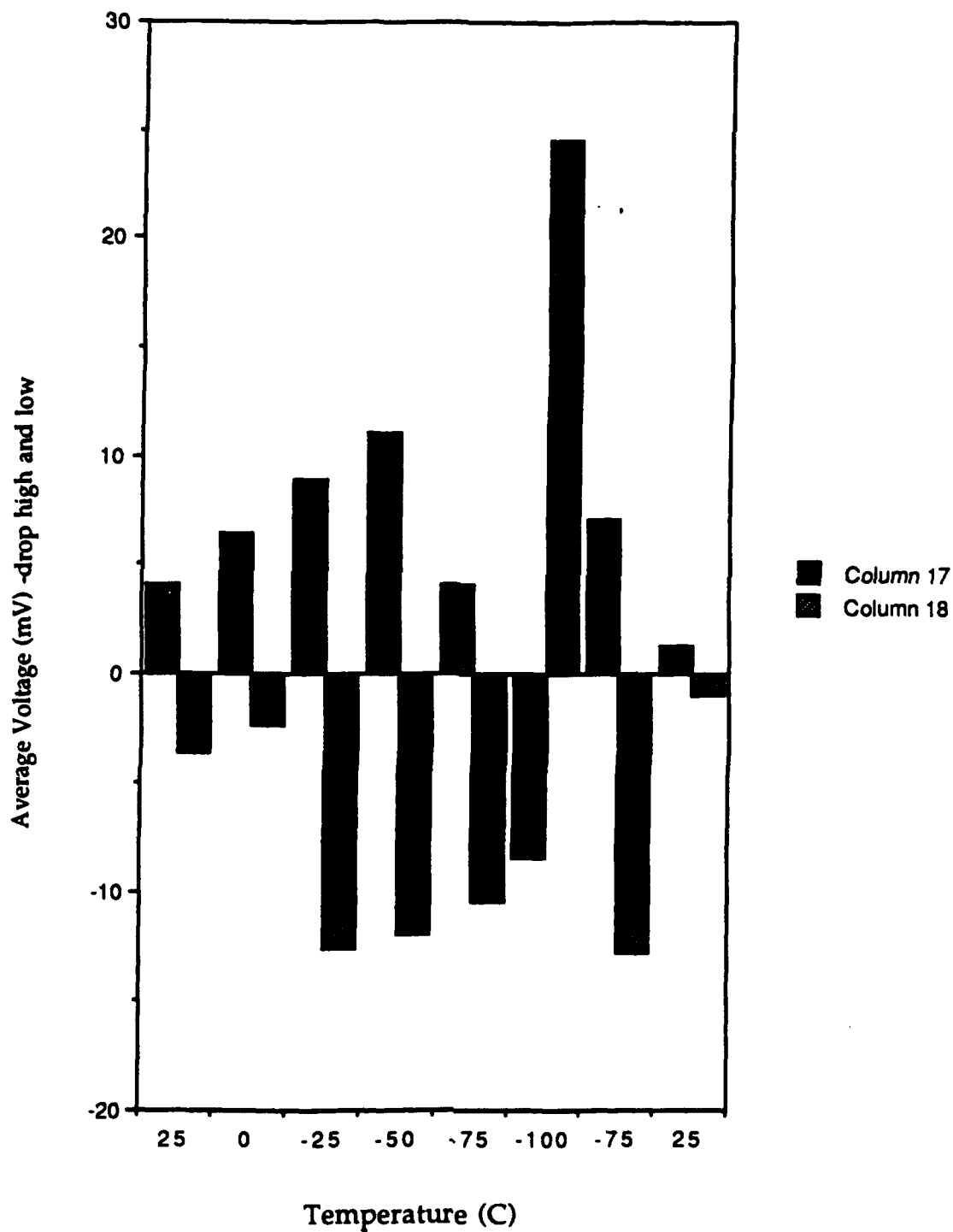


Figure 15

Average Open Circuit Voltages as Function of Temperature - 2 pairs of Ag/AgCl Electrodes in Butyronitrile and TMAC

**Figure 16**